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# Highly efficient recovery and clean-up of four heavy metals from MSWI fly ash by integrating leaching, selective extraction and adsorption



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## ABSTRACT

Municipal solid waste incineration (MSWI) fly ash contains significant amounts of heavy metals (e.g., Cd, Cu, Pb and Zn) and is therefore considered to be a hazardous waste requiring proper treatment prior to its disposal. In this work, an integrated hydrometallurgical process for treatment of MSWI fly ash was evaluated. Valuable metals, e.g. Cu and Zn, were first recovered by combining leaching and extraction sequentially. In the next step, the t removal of Cd and Pb from the remaining leachate using four types of iron-based adsorbents was evaluated. The leaching was optimized with respect to pH, leaching time and liquid to solid ratio. A test done under optimal conditions gave metal releases of 100% and 80% for Cu and Zn as well as 100% and 85% for Cd and Pb, respectively. The resulting leachate was contacted with organic phases based on kerosene containing the extractants LIX860N–I for Cu extraction and Cyanex 572 for Zn extraction in two consecutive steps. Efficient extractions were achieved, thus demonstrating that the combination of leaching and extraction can be successfully used for the recovery of Cu and Zn. Adsorption of heavy metal ions on various iron based sorbents to detoxify the aqueous effluent from the extraction showed good removal efficiency (more than 95%) for both Cd and Pb. The results of this study show that the proposed integrated process is a promising tool that can be used in the strategy for metal recovery and detoxification of MSWI fly ash.

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# 1. Introduction

Over the past few decades, incineration has become a widely

prevalent alternative for municipal solid waste management all over the world (Song et al., 2017), due to the energy recovery and reduction in the volume and mass of waste (Narayana, 2009). However the MSWI process produces a considerable amount of fly ash which is commonly rich in leachable heavy metals, thus posing a serious threat to the environment and human health. Fly ashes have been classified as a hazardous waste (MEE, 2016), which must

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be treated properly to prevent environmental pollution (Garcia-Lodeiro et al., 2016).

China is one of the largest municipal solid waste producing countries in the world. It is reported that the MSW generated was approximately 170 Mt in 2016, with an annual increase of 8–10% (Xin-gang et al., 2016). Meanwhile, for the aim of proper treatment, the proportion of incineration in the waste disposal (waste to energy) will be increased from 31% in 2015 to 54% in 2020 in China according to the "13th Five-Year" National Municipal Solid Waste Disposal Facilities Construction Plan. The amount of municipal solid waste incineration fly ash generated will increase rapidly as a consequence. However, only a few landfill sites designed for the disposal of hazardous waste like MSWI fly ash in China are now in service (Cheng and Hu, 2010) while the construction of new sites lags behind the construction of incineration plants. Therefore, it is urgent to drive the processing options available due to the huge capacity gap.

So far, a number of technologies have been developed for the disposal of fly ash. The rationale most often used is to immobilize and/or stabilize the fly ash in matrices, such as a combined washing-immobilization process (Mangialardi, 2003), via cementation process (magnesium potassium phosphate (Su et al., 2016), red mud (Su et al., 2019a)), using low temperature sintering (Su et al., 2019b), or using mercapto functionalized dendrimer Chelator (Zhang et al., 2016) etc. However, a stabilization/immobilization process for fly ash treatment not only requires a great expense for the material disposal, but also results in a huge loss of valuable metal resources that are contained in the fly ash (Li et al., 2014). From an environmental and economic perspective, it is of great significance to recover these valuable resources. A hydrometallurgical process has distinct advantages in the treatment of fly ash, in which metals are low grade and present with many contaminants (Tang and Steenari, 2016). A handful of publications have reported that this technique can be used to recover a number of metals from fly ash, such as copper (Karlfeldt Fedje et al., 2012), zinc (Ko et al., 2013) and (Tang et al., 2017), nickel (Kuboňová et al., 2013), and lead (Tao et al., 2014). However, secondary waste (solid residue and effluents) generated during those process were seldom discussed. It has been reported that the treated solid products, e.g. the ash residues after leaching and bio-leaching (Funari et al., 2016), or fly ash after sintering (Liu et al., 2009), still release significant amounts of heavy metals during the toxicity characteristic leaching procedure (TCPL) and do have an effect on environment. Meanwhile, reports about work on the subsequent treatment to process those secondary waste forms were very rare (Venäläinen and Hartikainen, 2018).

The use of bare iron-based nanomaterials is readily considered as an alternative for contaminated water remediation. However, they are often susceptible to easy agglomeration and unstable due to the nanometer size effect (Zhu et al., 2012). Furthermore, they are easily oxidized in air and corroded in an aqueous solution with low or high pH value thus leading to a decreased activity. To cope with this problem, it is commonly coated with hydrophobic stabilizers, such as carboxymethyl cellulose (Jiang et al., 2014).

In the work presented in this paper, a hydrometallurgical route, consisting of three steps, i.e. leaching, solvent extraction and adsorption, to realize metals recovery from fly ash and detoxification of secondary waste streams, was developed. The importance of this work is the use of real MSWI fly ash and the comprehensive treatment of fly ash and derived secondary waste streams. And a flowsheet for the integrated of metal recovery and subsequent treatment of waste effluents is presented.

# 2. Experimental

As presented in Fig. 1, the comprehensive treatment of MSW fly

ash suggested consists of three steps: acidic leaching, Cu and Zn recovery and removal of toxic metals from secondary effluents. It should be noted the Cu extraction and Zn extraction should be carried out sequentially since Cyanex 572 could extract Cu as impurity during Zn extraction.

### 2.1. MSWI fly ash sample, chemicals

All inorganic reagents used were of analytical or higher grade purity and purchased from Sigma Aldrich and deionized (DI) water was used throughout this study. The extractants LIX860N-I and Cyanex 572 as well as the kerosene diluent used are commercially available. The fly ash was collected from an MSW incineration unit based on the fluidised bed combustion technology during normal operation. Eight fly ash samples were collected every day for 2 weeks and then thoroughly mixed into a general sample that was kept in an air tight plastic container. From this general sample the sample used in this work was taken out using standard sample diving equipment (Rittler divider). To determine the element concentrations in the ash, the ash sample was treated by acid digestion in a solution including HF (bomb dissolution) until complete dissolution. The method has been developed to dissolve the whole sample including silicates and these standardized analyses were carried out by an accredited laboratory.

# 2.2. Process evaluation

## 2.2.1. Leaching of fly ash

The leaching behavior of heavy metals in the fly ash sample was examined through a constant-pH leaching test (CPLT) at ambient condition ( $25 \,^{\circ}$ C). Fly ash samples were leached for up to 70 h with magnetic stirring using hydrochloric acid (>37%, Sigma Aldrich) with fixed liquid to solid (L/S) ratio up to 30 (v/w of 7, 14 and 30, respectively). The solution pH was kept at 2, 3 and 4 respectively using a constant pH titration instrument (Metrohm, 905 Titrando).

The leachate was sampled at times for metal concentration analysis, a 0.45  $\mu$ m syringe filter was used to withdraw and filter 5 mL of leachate and the metal concentrations were determined using Inductively Coupled Plasma-Mass Spectrometry ICP-MS (iCAP Q, Thermo Fischer) with a satisfactory calibration line (R<sup>2</sup> = 0.9999 for Cd and Cu, R<sup>2</sup> = 0.9997 for Zn and R<sup>2</sup> = 0.9995 for Pb, respectively). The non-dissolved ash residues remaining after the tests were filtered and dried for use in the landfill criteria evaluation.

# 2.2.2. Landfill criteria for leaching residue

The preliminary evaluation of leaching residue for admission on a landfill, was made using the compliance leaching test (BS EN 12457–2: 2002). The tests were carried out at L/S = 10 (v/w) at ambient temperature and the ash residue was contacted with deionized (DI) water (MilliQ, Millipore, >18 MΩ/cm) for 24 h. Aliquots of supernatant solutions were sampled for analysis and comparison with the landfill criteria (EU, 2003/33/EC) (EU, 2002). The element concentrations in these samples were determined by ICP-MS after centrifugation and filtration.

#### 2.2.3. Extraction of metals from leachates

The batch tests were carried out in 3.5 mL glass vials sealed with plastic lids. The experiments were performed in a thermostatic shaking machine (IKA VXR basic Vibrax) with vibration speed 1500 vpm at ambient temperature (25 °C). Copper extraction was carried out using LIX860N–I, (Cognis), followed by zinc extraction using Cyanex 572 (Cytec) as extractant. Both extractants were diluted to 1 mol/litre solutions in kerosene (Solvent 70, Statoil). Based on results from a previous study (Tang et al., 2018c), a leachate pH of 4



Fig. 1. Schematic of the overall evaluation process for the recovery and clean-up of four heavy metals from MSWI fly ash. This study starts with the Cu, Zn recovery by combining leaching and solvent extraction, followed by disposal of secondary waste streams (landfill criteria for residue and emission criteria for effluent). The experimental parameters are presented as subtitle in each procedure.

was used since this pH level is most suitable for the extractants. In addition, a time of 5 min for contact between the leachate and the organic phases and an organic to aqueous (O:A) ratio of 1:1 (v/v) was chosen for all extraction experiments. The resulting CPLT leachates (pH 2, 3, and 4 respectively) were adjusted to pH 4 by adding a very small amount of 1 M sodium hydroxide solution.

After the sequential extraction, the Cu-loaded organic and Znloaded organic phases were mixed with sulfuric acid and hydrochloric acid respectively for test of stripping method. The stripping experiments were carried out for 5 min with a volume ratio between the organic phase and the acid solution (O:A v/v) of 1. The pH values of the effluents (to corresponding CPLT leachates) were adjusted to 2, 3 and 4 by adding 1 M hydrochloric acid or 1 M sodium hydroxide solution for the adsorption investigation. The metal concentration in aqueous phase were analyzed before and after extraction using ICP-MS, and the amounts of metal ions extracted by the organic phase were calculated using the mass balances. When the metals Cu and Zn have been transferred to a new aqueous phases in the stripping steps they can be recovered in pure form by electrowinning which is a standard metallurgical method.

## 2.2.4. Effluent decontamination

Decontamination, i.e. removal of toxic metals in this work represented by Cd and Pb, of the aqueous phases remaining after electrowinning of Cu and Zn is in this work suggested to be carried out by using an adsorbent (Fig. 1). The adsorption tests were one-stage batch experiments performed in closed glass vials in triplicate. The experiments were carried out in a thermostatic shaking machine at ambient temperature (25 °C). The influencing factors: adsorbent type (i.e. bare nano zerovalent iron (nZVI) and carboxymethyl cellulose decorated zerovalent iron (CMC-nZVI), as well as bare magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) and humic acid coated magnetite (HA-Fe<sub>3</sub>O<sub>4</sub>), initial pH (2, 3 and 4 respectively) and contact time (30 s - 24 h) on the adsorption process were investigated. The equilibrium adsorption capacity  $Q_e$  (mg/g) of Cd and Pb was calculated as Eq. (1), expressed as:

$$Q_e = \frac{(C_0 - C_e)}{m} \cdot V \tag{1}$$

where  $C_0$  and  $C_e$  (mg/L) are the initial and equilibrium metal

concentration in solution, respectively; m is the mass (g) of adsorbent and V (L) is the solution volume.

Effluents were the aqueous solution obtained from Zn extraction. Four adsorbents, nZVI and CMC-nZVI, as well as bare  $Fe_3O_4$  and humic acid coated magnetite (HA-Fe<sub>3</sub>O<sub>4</sub>) were prepared following the procedure reported in literature (Liu et al., 2013) for former two and (Rashid et al., 2017) for latter magnetites, respectively.

All the solid products, nZVI, CMC-nZVI, Fe<sub>3</sub>O<sub>4</sub> and HA-Fe<sub>3</sub>O<sub>4</sub> were washed with pure water several times and dried in a vacuum oven at 40  $^{\circ}$ C. The final vacuum dried particles were ground and stored in a vacuum desiccator.

2.2.4.1. Adsorption kinetics and dependency of pH. Adsorbent dosages of 10 g/L of nZVI, CMC-nZVI, Fe<sub>3</sub>O<sub>4</sub> and HA-Fe<sub>3</sub>O<sub>4</sub> respectively, were used to study the effect of effluent pH on the adsorption. The effluents described in Table 3 with initial pH in the range of 2–4 were used as aqueous solutions. The experiments were carried out at 25 °C. The adsorption time was in the range of 0.5 min–24 h (0.5 min, 1 min, 5 min, 10 min, 15 min, 30 min, 45 min, 60 min, 1.5 h, 2.0 h, 2.5 h, 3.0 h, 6.0 h, 12 h and 24 h). Test results were examined using linear fitting with pseudo-first order and pseudo-second

Table 1

Contents of elements in the investigated fly ash, determined by dissolution of fly ash in concentrated acids. Nd means not detected.

Elements	Content/mg/kg	Elements	Content/mg/kg
Al	20,000	As	80
Ca	360,000	Ba	770
Fe	5600	Cd	90
K	25,000	Со	20
Mg	10,000	Cr	190
Na	32,000	Cu	5400
Р	4000	Hg	3
S	7000	Mn	570
Si	32,700	Mo	10
Ti	1800	Ni	30
Cl	200,000	Pb	5700
		Sb	nd
		Se	nd
		Sn	20
		V	10
		Zn	5800

#### Table 2

Concentrations of selected ash elements in leachates obtained at different pH (25  $\pm$  1 °C, 20 h, L/S = 14 v/w), all results are given in mg/L. Nd = not detected.

Element	$CPLT \ pH = 2$	$CPLT \ pH = 3$	$CPLT \ pH = 4$
Al	801 ± 11	$644 \pm 4$	$114 \pm 4$
Ca	18,200 ± 283	17,300 ± 617	$18,400 \pm 334$
Cd	$6.4 \pm 0.2$	$6.4 \pm 0.3$	$6.4 \pm 0.2$
Cr	$4.9 \pm 0.2$	$3.5 \pm 0.1$	Nd
Cu	$386 \pm 5$	$365 \pm 2$	$359 \pm 2$
Fe	$165 \pm 1$	$123 \pm 0$	$46.4 \pm 1$
К	$1670 \pm 21$	$1710 \pm 18$	$1790 \pm 20$
Mg	$539 \pm 9$	$519 \pm 2$	$506 \pm 5$
Mn	$29.9 \pm 0$	$26.8 \pm 0$	$28 \pm 0$
Na	$1570 \pm 21$	$1580 \pm 39$	$1530 \pm 18$
Pb	$351 \pm 6$	$345 \pm 5$	$346 \pm 4$
Si	$1240 \pm 21$	$979 \pm 12$	$88.7 \pm 2$
Ti	$3.7 \pm 0.4$	Nd	Nd
Zn	$349 \pm 3$	$317 \pm 2$	$301 \pm 1$

#### Table 3

The yield of recycled Cu and Zn from leachate. All results are presented in % of the concentration in the leachate.

	Cu	Zn
Extraction Stripping Totally	$\begin{array}{c} 100.0 \pm 0.1 \\ 95 \pm 0.3 \\ 95 \pm 0.3 \end{array}$	$91 \pm 2$ $91 \pm 1$ $82 \pm 2$

order kinetic models (Eq. (2) and Eq. (3), respectively), to study the adsorption mechanism.

$$\log(Q_{\ell} - Q_{t}) = \log Q_{\ell} - \frac{k_{1}}{2.303}t$$
(2)

where  $Q_e$  (mg/g) and  $Q_t$  (mg/g) are the adsorption capacities at equilibrium and at contact time *t* (min), respectively, whereas  $k_1$  (h<sup>-1</sup>) is the rate constant at equilibrium.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t$$
(3)

where  $k_2$  (h<sup>-1</sup> g mg<sup>-1</sup>),  $Q_t$  (mg·g<sup>-1</sup>), and  $Q_e$  (mg·g<sup>-1</sup>) are the second-order rate constant for adsorption, adsorption at contact time *t* (min), and amount of adsorption at equilibrium.

After selecting a proper adsorption condition based on former experiment (adsorbent, contact time and pH were chosen as CMC-nZVI, 3 h and pH of 4 respectively)., the influence of adsorbent dosage (1, 2, 5, 10 and 20 g/L) and reaction temperature (25 °C, 40 °C and 60 °C) were investigated.

*2.2.4.2. Effect of adsorbents dosage.* Adsorbent with dosage of 1, 2, 5, 10 and 20 g/L were added into the 25 mL effluent solution of pH 4 respectively. The contact time was 3 h to ensure that the equilibrium was reached.

2.2.4.3. Effect of temperature on adsorption. Effect of temperature on adsorption was investigated at temperatures  $25 \,^{\circ}$ C,  $40 \,^{\circ}$ C and  $60 \,^{\circ}$ C by adding adsorbent with  $10 \,$ g/L to the  $25 \,$ mL effluent of pH 4 solution. The contact time was 3 h.

### 2.2.5. Emission criteria for treated effluent

The aqueous solutions after adsorption were separated from adsorbents using a handheld magnet, those magnetically separated solutions were then centrifuged and further filtered (polypropylene syringe filter, 0.45  $\mu$ m). The filtrates were analyzed using ICP-MS (iCAP Q, Thermo Fischer) and assessed with respect to GB 31573–2015 (MEE, 2015).

## 3. Results and discussion

The contents of main and trace elements the fly ash determined after total dissolution of an ash sample taken from the ash bulk according to an accredited procedure are given in Table 1. The analysis uncertainties in the data given by the laboratory are  $\pm 25\%$ . Since the composition of MSWI fly ash varies over time due to variations in the fuel composition and variations in process conditions the data given here should be seen as an example of the composition of an ash coming to a treatment plant.

## 3.1. Leaching experiments

Effective dissolution of metals in ash needs acidic leaching, which means that alkaline compounds, such as CaO, Ca(OH)<sub>2</sub> and CaCO<sub>3</sub>, have to be neutralized. To estimate the acid consumption for the dissolution of metal compounds, the quantity of proton equivalents required to reach and maintain the desired pH during experiment was calculated and presented in Fig. S1. For example, leaching solutions of pH 2 and pH 4 require 14.1 and 13.3 mmol H<sup>+</sup>/ g of ash, respectively. Increasing acidity from pH 4 to 2 may have positive effect on fly ash dissolution (Tang and Steenari, 2016).

## 3.1.1. Dependency of leaching pH and kinetics

To obtain an understanding of the process kinetics at different pH, leaching was monitored at 25  $^{\circ}$ C for an L/S ratio of 14. The overall leaching behavior is given in Fig. S2, and shows that the acid consumption was fast in the first 10 min and that an equilibrium was achieved within 2 h. The leaching behavior of Cd, Cu, Pb and Zn at pH 2 gave similar results (Fig. S3). Further leaching studies were thus carried out at 25  $^{\circ}$ C.

The results shown in Table 2 indicated that pH plays an important role in the release of metal ions from the ash. An increased acidity (pH 4 to 2) increased the yield of Zn from 72% to 84% and of Cu from 93% to 100%. It also led to a significantly higher dissolution of Al (8%–56%), Fe (11%–41%) and Si (4%–53%), which may be a problem since Fe is an undesired impurity that consumes extractant during the zinc extraction step (Tang and Steenari, 2015). In addition, high concentrations of Al and Si in the leachate can give aprecipitation of pyrophyllite (Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>) and gel formingation. Some elements, such as Ca, Cd and Pb in fly ash occur mainly in acid soluble forms resulting in a similar leaching behavior in given conditions.

## 3.1.2. Effect of liquid to solid ratio

Liquid to solid ratios (L/S) of 7, 14 and 30 v/w were studied using the hydrochloric acid system with pH 2. Increases in L/S ratio generally led to a faster dissolution of metals initially (Fig. 2) but similar efficiency when reaching equilibrium for the four metals studied. For Zn a slightly higher leaching efficeency, 93%, was achieved at L/S (v/w) of 30 compared to roughly 89% obtained at L/S (v/w) of 14.

Based on the results described above a leaching at constant pH with experimental conditions pH 2, L/S = 30 v/w and 70 h leaching time would give the best leaching efficiency for Cu, Zn, Cd and Pb. Considering that a leaching time of 70 h would probably be too long to fit in an industrial process and that a high liquid to solid ratio causes a higher flow of waste water and a more diluted leachate (Tang et al., 2018a), it was decided to use a CPLT with L/S = 14 v/w and leaching time 20 h as a suitable compromise for the continued experiments. If the recovery efficiency of Cu and Zn is prioritized the leaching should be performed at pH 2 but if removal of Cd and Pb is also required at pH of 4 should be used. The pH 4 leaching also gives lower leachate concentrations of other elements, such as Fe and Si which can interfere in the zinc extraction and cause



Fig. 2. The leaching behavior of metals (a) Cd, (b) Cu, (c), Pb, (d) Zn at 25 °C with hydrochloric acid solution (CPLT with pH = 2, L/S ratios of 7, 14 and 30 v/w).

# precipitation and filtration problems.

## 3.2. Characterization of residue

The stability of the leaching residue described in Table S1 towards leaching in water was evaluated by the landfill compliance leaching test (BS EN 12457–2: 2002). By comparing the results to the limiting values, the residue could be acceptable for landfilling at a regular site. The overall acceptance of metal leaching of the residue is a clear advantage over the original fly ash, which has to be deposited at specific hazardous landfill sites with a high expense (Zhao et al., 2016).

## 3.3. Extraction of Cu and Zn in leachate

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Two commercial extractants were screened: LIX860N–I (5nonyl-salicyl-aldoxime) (Cognis, 2014) for Cu extraction (Tang and Steenari, 2015), and Cyanex 572 (a mixture of phosphinic (H<sub>2</sub>P(=O)OH) and phosphonic acids (HP(=O) (OH)<sub>2</sub>)) (Cytec, 2014) for Zn extraction (Tang et al., 2018b). The general extraction mechanism can be expressed by equation (Eq. (4)).

$$M_{aq}^{2+} + 2HA_{org} \leftrightarrow MA_{2org} + 2H_{aq}^{+}$$
(4)

where M represents Cu or Zn, HA is either LIX860N–I or Cyanex 572.

Cu and Zn mono solutions were obtained via extraction and stripping, and the performance of the extractions are presented in Table 3. For the Cu recovery, the efficiency of extraction and stripping were 100% and 95%, respectively. The efficiency of Zn

extraction and stripping were 90% and 91%, respectively. In total, 95% of the copper and 82% of the zinc in the leachates could be recovered.

# 3.4. Adsorption of cadmium and lead in the effluent

The decontamination of the secondary aqueous waste stream, i.e. the effluent generated after the zinc extraction (Fig. 1) was studied. Removal of heavy metals, here exemplified by Cd and Pb (Table 4) by an adsorption process was performed. Other released elements are omitted from this table for simplicity. To study the pH influence on the removal of Cd and Pb, three solutions where the pH levels were adjusted to different values (2, 3 and 4, respectively) were used.

## 3.4.1. Adsorption kinetics and dependency of pH

The adsorption behavior of Cd was first investigated and the results for reaction times up to 24 h in the pH range of 2–4 are presented in Figs. 3 and 4, respectively. The results reveal that the adsorption efficiency is highly dependent on the solution pH as well as on the properties of the sorbents. All four systems reached

Table 4

Composition of the effluents used in the adsorption study. The effluents were obtained after Zn extraction with pH adjustment.

Element	Effluent (mg/L)	Effluent (mg/L)	Effluent (mg/L)
	pH = 2	pH = 3	pH = 4
Cd	$6.4 \pm 0.2$	$6.4 \pm 0.3$	$6.4 \pm 0.2$
Pb	$350 \pm 5.7$	$345 \pm 4.5$	$346 \pm 4.5$

equilibrium for Cd adsorption within 3 h under the experimental conditions. Particularly, the adsorption system using nZVI as adsorbent reached the equilibrium within 45 min and gave a removal rate of 71% at pH of 2, and the CMC-nZVI adsorption systems were even faster, probably due to that the CMC acted as a stabilizer that inhibited oxidation and aggregation of the nZVI. The equilibrium was reached in less than 30 min and the removal yield was markedly promoted comparing to the bare nZVI system (from roughly 70%–95% at pH of 2). Similar results have been obtained in the work of He and co-workers (He et al., 2007) and in the work of Zhou (Zhou et al., 2014). The removal efficiency was improved as well since the presence of humic acid inhibited the particle aggregation of unmodified magnetite (Illés and Tombácz, 2006). More than 80% of Cd could be removed using HA-Fe<sub>3</sub>O<sub>4</sub> while only 60% of Cd was removed by bare Fe<sub>3</sub>O<sub>4</sub> particles. It was also noted that the HA coating slowed down the equilibrium reaction and it took approximately 2 h for HA-Fe<sub>3</sub>O<sub>4</sub> adsorption system to reach the equilibrium.

The adsorption of Pb was similar to that of Cd. As shown in Fig. 4, the adsorption equilibrium was reached within 3 h. The bare nZVI and CMC-nZVI gave equilibrium adsorption yields of 72% and 94%, respectively. The Pb removal yield of the HA-Fe<sub>3</sub>O<sub>4</sub> system was slightly higher than that of the bare Fe<sub>3</sub>O<sub>4</sub> system.

The removal efficiency of Cd and Pb was low at the lower pH and promoted by an increase of pH using both bare nZVI and bare  $Fe_3O_4$ particles. The same trend of pH dependence for Cd adsorption using nZVI and  $Fe_3O_4$  particles has been reported earlier (Boparai et al., 2013). In a strongly acidic medium, there is a possibility of nZVI and  $Fe_3O_4$  dissolution and thus decrease in the activity and number of binding sites for adsorption. Other researchers have reported that the Cd adsorption is mainly due to chelating by -OH groups at the surface of the iron oxide, adsorption, and precipitation as hydroxides (Su et al., 2014). Therefore, this process is promoted by the decreased concentration of protons (H<sup>+</sup>) in the solutions. The specific removal mechanisms involved in the removal of Cd and Pb using iron-based materials mainly depends on the standard redox potential (Lide, 2006). Cd (E<sup>0</sup> -0.40 V, 25°) has a potential very close to that of Fe (E<sup>0</sup> -0.41 V, 25°), thus the removal of Cd is caused by adsorption (Li and Zhang, 2007). Pb (E<sup>0</sup> -0.13 V) has a slightly more positive potential than Fe, which means that it could be removed via reduction to Pb<sup>0</sup> (O'Carroll et al., 2013), and by adsorption as Pb<sup>2+</sup> (Xi et al., 2010). In addition, Pb<sup>2+</sup> can react with nZVI and precipitates to form Pb(OH)<sub>2</sub>, which further oxidizes to  $\alpha$ -PbO<sub>2</sub>(-Tosco et al., 2014).

The results reveal that CMC and humic acid coatings on the iron oxides could enhance the removal efficiency under experimental conditions, especially at high acidity. The removal of Cd and Pb using CMC-nZVI can be as high as 99% for Cd and Pb at pH of 4. The removal rate using HA-Fe<sub>3</sub>O<sub>4</sub>, observed from Figs. 3 and 4 gave an efficiency of 82%–88% for Cd and 84%–93% for Pb, indicating that the surface modification of iron-based nanoparticles might enhance their adsorption capacity.

By plotting the log ( $Q_{e,expt} - Q_{f}$ ) versus time, parameters of a pseudo first order model,  $k_1$  and  $Q_{e, cal}$  could be calculated by the slope and intercept of log ( $Q_e - Q_f$ ). As presented in Fig. 5 and Table S2, it is can be observed that the fittings are non-linear when plotted in this manner. The agreement between  $Q_{e, expt}$  from experiments and  $Q_{e cal}$  based on the calculation using Eq. (2) is very poor for both Cd and Pb (Table S2). Therefore, it can be inferred that the adsorption of Cd and Pb on those four systems did not follow the pseudo first-order kinetics.

The parameters of pseudo second order, Qe. cal and K2 are



**Fig. 3.** Kinetics of Cd removal during the adsorption using 10 g/L adsorbent in the adsorption systems (a) nZVI, (b) CMC-nZVI, (c) Fe<sub>3</sub>O<sub>4</sub>, (d) HA-Fe<sub>3</sub>O<sub>4</sub> (Initial pH = 2, 3 and 4). Standard deviation was based on triplicate tests.



Fig. 4. Kinetics of the Pb removal during the adsorption using 10 g/L adsorbents in the adsorption systems (a) nZVI, (b) CMC-nZVI, (c) Fe<sub>3</sub>O<sub>4</sub>, (d) HA-Fe<sub>3</sub>O<sub>4</sub> (Initial pH = 2, 3 and 4). Standard deviation was based on triplicate tests.



**Fig. 5.** Pseudo first order kinetic model fit for **(a)** Cd and **(b)** Pb at ambient temperature (298.15 K). (Adsorption conditions: pH = 4, initial concentration of Cd,  $C_{0,Cd} = 6.4$  mg/L and Pb,  $C_{0,Pb} = 350$  mg/L, adsorbents dosage of 10 g/L).

presented in Fig. 6 and Table S3 by plotting  $t/Q_t$  versus t expressed in Eq. (3). The experimental  $Q_{e, expt}$  and calculated  $Q_{e, cal}$  are in good agreement. Furthermore, the correlation coefficients ( $R_2^2$ ) of pseudo second order kinetic model are close to 1 for both Cd and Pb respectively. The good fitting between  $Q_{e, cal}$  and  $Q_{e, expt}$  together with the high correlation coefficients reveal that both adsorption of Cd and Pb probably follow pseudo second order kinetics. These results indicated that Cd and Pb were adsorbed via the chemical interaction route. Similar results have been reported for the adsorption of both metal ions onto other adsorbents (Li et al., 2005).

#### 3.4.2. Dosage of adsorbent

The effect of absorbent dosage is presented in Fig. 7. It could be observed that the increase of the adsorbent dosage enhanced the adsorption yield significantly in all four systems. The adsorption of Cd improved from roughly 40%–99%, and for Pb there was an improvement in adsorption yield from 20% to 99% when increasing the CMC-nZVI dosage from 1 g/L to 20 g/L.

## 3.4.3. Effect of temperature on adsorption

The effect of temperature on the adsorption efficiency of the used adsorbents is shown in Fig. 8.



**Fig. 6.** Pseudo second order kinetic model fit for (a) Cd and (b) Pb at ambient temperature (298.15 K). (pH = 4, Adsorption conditions: initial concentration of Cd, C<sub>0.Cd</sub> = 6.4 mg/L and Pb, C<sub>0.Pb</sub> = 350 mg/L, adsorbents dosage of 10 g/L).



Fig. 7. Effect of absorbent dosage on the (a) Cd and (b) Pb removal. Standard deviations represent triplicate tests. Adsorption was performed for 3 h at 25 ± 1 °C with initial pH value of 4.



**Fig. 8.** Adsorption of **(a)** Cd and **(b)** Pb at 25 °C, 40 °C and 60 °C, respectively. Standard deviation was based on triplicates. Adsorption was performed for 3 h with initial pH value of 4. Dosage = 10 g/L.

The parameters of the pseudo second order kinetic for Cd and Pb adsorption using CMC-nZVI at various temperatures are presented in Table S3, respectively. The calculated adsorption capacity ( $Q_{e. cal}$ ) for Cd and Pb has the lowest values at 298.15 K in the studied experiment range and increases with increasing temperature, which reveals an endothermic reaction. Regarding the rate constant ( $K_2$ ), it could be seen from the results that the higher temperature gives a higher rate constant and thus a higher adsorption rate. A

#### Table 5

Removal of Cd and Pb from fly ash in the leaching/extraction (CPLT pH=4) –adsorption (pH=4) procedure outlined in Fig. 9 using CMC-nZVI (20 g/L) as adsorbent, all results are presented in % of the content in the original ash sample.

	Cd	Pb
in % of the metal content in the ash sample		
Leaching	$100 \pm 0.2$	$85 \pm 1$
Extraction	_	_
Adsorption	$100 \pm 1$	$100 \pm 2$
Totally	$100 \pm 1$	$85 \pm 2$

general conclusion based on the results of Fig. 8 and Table S3 is that a rise in experimental temperature leads to a higher adsorption capacity and faster rate in the studied range, revealing that the processes are endothermic, which agrees well to the literature for Cd (Boparai et al., 2011) and Pb (Jabeen et al., 2013).

## 3.5. Summary of the process

By integrating the three parts of the process for MSWI fly ash treatment which has been presented in Fig. 1: leaching, sequential extraction and adsorption, the results from the overall clean-up process for the recovery of Cu and Zn, as well as the removal of heavy metals (Cd and Pb) from the effluent is presented in Table 5 and Fig. 9. The adsorption efficiencies 99.8% for Cd and 99.9% for Pb could be obtained by adjusting the effluent pH to 4. High efficiencies were achieved for both leaching/extraction (Cu and Zn) and adsorption (Cd and Pb) experiments on bench scale.

## 3.6. Analysis of treated effluent

The results from a comparison between the metal concentrations in the treated effluent (Cd, Pb depleted aqueous phase in Fig. 9) and the corresponding limiting value for emission (Standard, GB 31573–2015) are presented in Fig. 10. The comparison shows that the resulting aqueous phase coming from the treatment process described in Fig. 9 has lower Cd and Pb concentrations than the limiting values. This indicates that the treated effluent might be acceptable for emission as far as Cd and Pb are concerned. Considering that the results obtained in the present work are promising, further work should be carried out on a larger scale investigation of the removal effect of suggested process on other heavy metals and other contaminating chemicals.

## 3.7. Preliminary flowsheet

An integrated hydrometallurgical production flowsheet to recover metals from MSWI fly ash and decontaminate the consequential secondary waste streams investigated here is presented in Fig. 11. The process consists of a leaching stage, this is aimed to dissolve Cu, Zn and other heavy metals (Cd, Pb). The resulting leachate undergoes a sequential solvent extraction stage, in which the Cu and Zn are effectively and selectively extracted by using LIX860N–I and Cvanex 572 respectively. The organic phase could be reused in process after washing or cleaning with e.g. water. Two secondary waste streams were produced, leaching residue and extraction effluent. Leaching of heavy metals from fly ash can lead to a safe enough solid residue which could be landfilled as a nonhazardous waste, and thus lower the management costs for this solid residue. Effluent containing heavy metals undergoes an adsorption stage with iron-based adsorbents, and the heavy metals, such as Cd and Pb are minimized in the solution. The loaded adsorbents could be easily separated from solution, subsequently regenerated with double distilled water washing and returned back to the process. Considering the overall bench experiments, it is thus possible to integrate the metal recovery and decontamination using a combined leaching, solvent extraction and adsorption. Effective extraction and stripping can be carried out continuously in a several stage mixer-settler system and the adsorption of other contained metals, like Cr, Ni, etc, in the effluent should be also



Fig. 10. Cd and Pb concentration in effluent after adsorption using CMC-nZVI and emission standards of limit values (GB 31573–2015) (MEE, 2015).



Fig. 9. Simplified mass flow of the integrated leaching-extraction-adsorption process, for Cu and Zn recovery from ash, as well as the removal of heavy metals Cd and Pb from secondary waste stream.



Fig. 11. Proposed flow scheme for the metal recovery from MSWI fly ash and the detoxification of effluent (raffinate).

investigated in future.

# 4. Conclusions

The research presented here aimed to evaluate an integrated hydrometallurgical process that treat municipal solid waste incineration fly ash. Heavy metals (Cu and Zn) can be effectively and selectively recovered via a leaching and solvent extraction process. Enhanced leaching gave a yield of 100% of the Cu and more than 75% of the Zn in the fly ash, as well as good leaching rates for Cd (100%) and Pb (85%), respectively. The leachates are then introduces as feed for copper and zinc extraction sequentially. The overall recovery yields for Cu and Zn were 95% and 70% under optimum conditions. The resulting leaching residue was assessed with landfill compliance leaching test and it was acceptable to be landfilled in a regular non-hazardous waste landfill site. The extraction effluent was decontaminated by adsorption. The adsorption performance showed that CMC-nZVI gave a high and fast removal of both Cd (approximately 97%-99%) and Pb (94%-99%). The equilibrium could be reached within 30 min under the experimental conditions. The findings of this study demonstrated that this comprehensive process integrating leaching, solvent extraction and adsorption can be a practical strategy for MSWI fly ash treatment. Further investigation, e.g. about the removal of other heavy metals (such as As, Cr, Sb) and the pH effect on the adsorption in a larger range is needed. The economic and environmental assessment of the process are also planned.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2019.06.198.

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